

滇姜花中的新二萜成分——滇姜花素 D^{*}

邹澄¹ 赵庆^{2**} 郝小江³ 陈耀祖⁴ 洪鑫³

(¹ 昆明医学院药理学系, 昆明 650031)

(² 云南中医学院药理学系, 昆明 650200)

(³ 中国科学院昆明植物研究所植物化学开放实验室, 昆明 650204)

(⁴ 兰州大学化学系, 兰州 730000)

摘要 从滇姜花 *Hedychium yunnanense* 根茎中分离到 3 个二萜成分, 分别为滇姜花 D (1), 圆瓣姜花素 A (2) 和 hedychenone (3), (1) 为新化合物, 其结构经波谱学方法鉴定为 13 β -furanolabda-6-oxo-7, 11-dien-17-ol。

关键词 滇姜花, 滇姜花素 D, 二萜

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Yunnancoronarin D, A New Diterpenoid from *Hedychium yunnanense*

ZOU Cheng¹, ZHAO Qing², HAO Xiao-Jiang³, CHENG Yao-Zu⁴, HONG Xin³

(¹ Faculty of Pharmacy, Kunming Medical College, Kunming 650031)

(² Faculty of Pharmacy, Yunnan Traditional Chinese Medical College, Kunming 650011)

(³ Laboratory of Phytochemistry, Kunming Institute of Botany, The Chinese Academy of Sciences, Kunming 650204)

(⁴ Department of Chemistry, Lanzhou University, Lanzhou 730000)

Abstract Three diterpenoids, yunnancoronarin D (1), forrestin A (2), and hedychenone (3) were isolated from the rhizomes of *Hedychium yunnanense* Gagnep. The first one is a new compound and its structure was elucidated as 13 β -furanolabda-6-oxo-7, 11-dien-17-ol by spectra methods.

Key words *Hedychium yunnanense*, Yunnancoronarin D, Diterpenoid

We reported a series of antitumor diterpenoids from plants of *Hedychium yunnanense* (Zhao *et al*, 1995a; Zhao *et al*, 1995b; Zhao *et al*, 1996) and *H. forrestii* (Zhao *et al*, 1995c). Further study on the rhizomes of *Hedychium yunnanense* resulted in the isolation of three labdane type diterpenoids including a new one. In this paper we describe the structural elucidation of the compounds.

RESULTS AND DISCUSSION

Dried and pulverized rhizomes of *Hedychium yunnanens* collected in district of Guandu, Kun-

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** To whom correspondence should be addressed

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ming, China, in 1993, were extracted with alcohol three times. The extract was further extracted with petroleum ether three times to give brown oil. Brown oil was purified by repeated column chromatography on silica gel and alumina to afford three diterpenes (1), (2) and (3).

Compound (1), colorless oil, $C_{20}H_{26}O_3$. The ^{13}C NMR spectrum gave 20 carbon signals, including one carbonyl (δ 200.1), eight olefinic carbons ($CH \times 6$, $C \times 2$), one hydroxymethyl carbon (δ 63.6). The 1H NMR spectrum indicated the presence of a hydroxymethyl (δ 4.03 and 4.12), a *trans* double bond (δ 5.69 and 6.35), and a β -substituted furan ring (δ 6.48, 7.34 and 7.39). The IR spectrum gave a sharp absorption band due to α , β -unsaturated ketone (1666 cm^{-1}), as well as a hydroxy (3418 cm^{-1}), gem dimethyl (1386 , 1377 , 1231 and 1160 cm^{-1}) and a furan (1507 , 871 and 780 cm^{-1}).

Table 1 ^{13}C NMR data of (1) ~ (3)

C	(1)	(2)	(3)	C	(1)	(2)	(3)
1	39.9	39.7	40.1	11	124.6	134.9	124.6
2	18.0	17.8	18.0	12	125.3	122.9	125.9
3	43.3	42.9	43.2	13	123.5	128.8	123.7
4	32.5	32.6	32.4	14	107.4	143.7	107.4
5	58.6	60.0	61.2	15	140.4	69.6	140.1
6	200.1	194.9	199.6	16	143.6	172.0	143.5
7	124.1	144.1	128.0	17	63.6	14.8	22.8
8	158.8	123.9	156.9	18	33.5	33.4	33.5
9	63.7	62.1	63.3	19	21.7	21.5	21.6
10	43.0	43.0	42.6	20	15.7	15.6	15.6

Table 2 1H NMR data of (1) ~ (3)

H	(1)	(2)	(3)
5	2.10 (1H, s)	2.09 (1H, s)	2.07 (1H, s)
7	6.09 (1H, s)		5.83 (1H, s)
9	2.98 (1H, d, 10.0)	2.88 (1H, d, 10.3)	2.89 (1H, d, 10.1)
11	5.69 (1H, dd, 10.0, 15.6)	6.65 (1H, dd, 10.3, 15.8)	5.74 (1H, dd, 10.1, 15.6)
12	6.35 (1H, d, 15.6)	6.22 (1H, d, 15.8)	6.34 (1H, d, 15.6)
14	6.48 (1H, s)	7.23 (1H, d, 2.04)	6.51 (1H, s)
15	7.34 (1H, s)	4.80 (2H, s)	7.35 (1H, s)
16	7.39 (1H, s)		7.40 (1H, s)
17a	4.12 (1H, d, 17.5)	1.68 (3H, s)	1.76 (3H, s)
17b	4.03 (1H, d, 17.5)		
18	0.94 (3H, s)	0.92 (3H, s)	0.94 (3H, s)
19	1.13 (3H, s)	1.10 (3H, s)	1.13 (3H, s)
20	1.16 (3H, s)	1.15 (3H, s)	1.16 (3H, s)

The ^{13}C and 1H NMR spectra of 1 were similar to that of hedychenone (3) (Zhao *et al*, 1995a), indicating (1) was a labdane type furanoid diterpene. Comparison of ^{13}C NMR spectra of (1) and hedychenone suggested that C-17 of (1) was substituted by a hydroxyl group, which was also confirmed by the presence of hydroxymethyl (δ 4.03 and 4.12) in 1H NMR spectrum. Thus the structure of (1) was elucidated to be 13 β -furanolabda-6-oxo-7, 11-dien-17-ol as shown

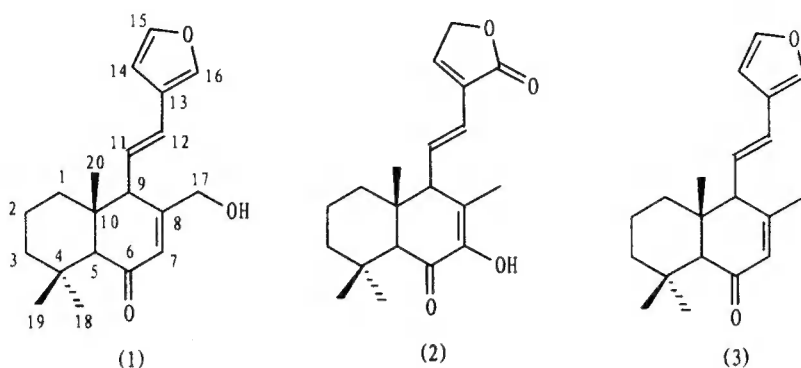


Fig.1 The structures of (1) ~ (3)

in Figure 1.

Compound (2) was identified as forrestin A, previously isolated from *H. forrestii* (Zhao et al, 1995c).

EXPERIMENT

General Mps. uncorr. Optical rotations were recorded on SEPA-300 with 2 cm cell. IR were taken with Perkin-Elmer 577. NMR were measured with AM-400 spectrometer using TMS as the internal standard. FAB-MS were determined with VG Autospec-3000 mass spectrometer.

Extraction and isolation The dried and pulverized rhizomes of *Hedychium yunnanens* (4.0 kg) collected in district of Guandu, Kunming, China, in 1993, were extracted with 95% EtOH three times at the reflux condition. The EtOH Extracts (410 g) was extracted with petroleum ether three times. Then the petroleum ether solutions were evaporated and got brown oil (230 g). The brown oil was separated into six fractions (Fr. A ~ F) by subjecting it to silica gel column chromatography (CC) using a petroleum ether-EtOAc gradient system. Fr. D was subjected to silica gel column chromatography eluting with petroleum ether-acetone (4:1) to give 518 mg of (2) as fine needles, together with a mixture. The mixture was further purified by alumina column chromatography eluting with CHCl_3 -EtOAc (4:1) to afford 31 mg of (1). Fr. A was recrystallized in cyclohexane-benzene (1:1) to give 8.2 g of (3) as needles.

Yunnan coronarin D (1) $\text{C}_{20}\text{H}_{26}\text{O}_3$, colorless oil, $[\alpha]_D^{20} + 76.42^\circ$ (c, 0.265, CHCl_3). $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3418, 1666, 1507, 1386, 1377, 1231, 1160, 871, 780. ^1H NMR and ^{13}C NMR; see Table 1 and 2.

Forrestin A (2) $\text{C}_{20}\text{H}_{26}\text{O}_4$, fine needles (benzene), mp is indefinite. $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400, 1743, 1665, 1640. ^1H NMR and ^{13}C NMR; see Table 1 and 2.

Hedychenone (3) $\text{C}_{20}\text{H}_{26}\text{O}_2$, needles (cyclohexane-benzene 1:1), mp $131.5 \sim 133^\circ\text{C}$. $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1660, 1500, 870, 790. ^1H NMR and ^{13}C NMR; see Table 1 and 2. (下转 259 页)

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